# UNCLASSIFIED

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CENERAL

The Proceedings of the Air Force Materials Laboratory Fiftieth Anniversary Conference on Corrosio: of Military and Aerospace Equipment, held In Denver May 23-25, 1967, have been issued.tll Some seventy papers covering all aspects of correston are regardered in their answers. The indiction ual papers were reviewed in the two previous DMIC Reviews on Larresian and Competibility dated October 11, 1957, and December 15, 1967.

A litersture survey on raindrop erosion has teen released by Redatone Assenat, (2) The survey concludes that rain erosion is expected to be very terious with most nose-come materials when the missile nose-come radius is leve than 0.5 feet and It is pessing through rain as velocities greater than 3000 ft/sec. Equations are available for estimeting the penetration of individual raindrops into ductile metals and ablating surfaces at velocities to 30,000 ft/sec. Rein-erosion damage apparently is reduced as the thickness of the molten ablative material on the nose cone is increased. Mose-cone spikes have been effective in reducing rain-erosion damage at 'wiccities of a few thousand feet per second.

The effect on corresion resistance of boronfiber strengthening of aluminum, copper, and nickel has been reported by Avco.(3) The boron either had no effect on, or slightly enhanced, the correston retes of these meterials in chloride solutions or in eir exidation. In addition, the aluminum-poron composites showed a somewhat greater corrosion rate in buffered solutions at pH 8 and a slightly decreased rate at pri 4 and 10 (as compared with those without boron). The presence of boron in nickel accelerated the corrosion in aluminum sulfate solutions.

The effect of inhibitors on the corresion of sluminum, magnesium, stainless steel, and titanium in MyO4 containing added mater has been studied at the Aerespace Corporation. (1) Corresion tests were conducted at 15.5 C (59.9 F) for periods ranging from 15 to 60 days. Amonium fluorosulfonate (M4503f) appeared to be the pest of the inhibitors investigated. Other promising inhibitors were phosphorus pentafluoride, phosphorus trifluoride, and potassium fluoresulfenate. The long-term effects of the inhibitors on corrosion performance and their effects on propellant performance were not studied.

impact data for aluminum and titanium alloys are being determined by McDonnell Douglas as part of a study on the engineering behavior of tankage meterials in liquid propellants. (3) Standard ASMA

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connects issued that 70 (1-1b) indicated that 2014-16 alcaims was not impact sensitive in MyCa. or liquid fluoring but was impact sensitive in Cify at temperatures between -50 C : -59 F) and the bolline point. -14 C (6.8 F). Modified WMA room-cue impact tests revealed that II-5A1-47 alloy was not impact sensitive in N-Og, but was impact sensitive at 42.5 ft-15 in Clfg at -14 C.

#### CORSOSION OF ALIMINAM ALLOYS

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#### General.

The effect of a delonized water rinse after sulfuric acid-sodium dithromate treatment on the achesive-bonding characteristics of 2024 aluminum has been studied by Picatinny Arsenal. (6) Limeratons greater than 15 minutes in dejonized mater at 60 C (140 F) produced an iridescent film on the aluminum and a subsequent loss in adhesive bondability. A hy grated oxide layer (AlcCo-3HO) 1000 A thick was found on the surface of these specimens. Multivalent compounds added to the water were found to preferentially absorb into the aluminum oxide and block the entrance of water, thereby preventing hydration of the oxide. The addition to the dejonized water (at pN below 5) of guittivatent compounds such as HySO4, MgSO4, CrC3, NagGrgO7, NagSC4, FeCl2, and FeCly was recommended to give good bonding surfaces. Alkaline compounds such as MariTD3, NagrT3, and KyCOn were not recommended because they attack and discotor the aluminum.

# Stress-Corresion Cracking

Research on an accelerated atress-corrosion, test for eluminum elloys is continuing at Kalser.(7) A continuous immersion in 1 percent KaCl-2 percent KyCryOy solution at pil 4 and 60 C was found to be effective in separating the tempers of 2024, 2219. and 7075 allows that exhibit borderline and maximum resistance to cracking in the short-transverse direction of fabrication. The salt-dichromate test made these separations in 1 week or less compared with 30 days in alternate immersion in 3.5 percent YaCl solution. C-ring specimens gave the best correlation between the two test methods. Tensile specimens (1/3-inch disseter) did not always give an accressive test in the sait-dichromate tests specifically with the tempers of the 2219 and 7075 alloys which exhibited borderline resistance to cracking.

Research on the exfoliation and stresscorrection characteristics of high-strength heattreatable siminum alloy plate has been summarized by Alcoa (8) Specimens were evaluated in marine and industrial atmospheric tests and in acidified

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Douelas Aircraft has studied the threshold stress levels to cause stress-corresion crecking in synthetic seawater alternate immersion tests of eluminum elloys 2014-76, X2021-78E31, 2024-781, 2219-T87, X7002-T6, 7039-T64, and 7106-T6,(9) Unwelded sheet and plate specimens of eli alluys did not crack in 500-hour tests at stress leadings of 75 percent of the vield strength (long-transverse direction). Unnote'ed and notched specimens of alloys in all other conditions also survived tests at 75 percent of yield strength except those listed belows

> As welded: 2014-76, 2021-78531, 2024-781 Postweld artificial ages 2014-76, 7106-76 Postweld solution treatment plus artificial equ: 2014-76, 2021-78631, 2219-787, 7039-T64, 7106-T6.

Alcoe has issued the first annual report on crack-initiation phenomena in the stress corresion of aluminum alloys.(10) Studies were made with tuning-fort specimens of 2219 and 7075 alloys exposed to NaCl-AlCla-HCl solution at pH 1. The only significant microstructural features that influenced crack initiation appeared to be grain shape, structural directionality, and recrystallization which control the orientation of the corresion-susceptible grein-boundary paths with respect to the stressing direction. No correlations could be obtained with constituent particles, zones and precipitates within grains, boundary precipitate particles, dislocations, or surface irrequiarities such as pits or scratches (except when they coincided with a grain boundary).

The role of dislocations in the stress-

corrosion cracking of aluminum alloys is being \*tudied at Rocketdyne.(11) Experiments have been conducted with 7075 alloy to relate dislocation mobility with the capacity of the T73 temper to plastically deform at the root of a notch, whereas the T6 temper does not readily deform. Tests at anmitted inade of 35 to 180 pounds have been con-"ducted in an Instron machine with V-notch Charpy specimens taken from the short-transverse and longitudinal orientations of the original forgings. "N" values calculated from the slope of a log-log minutes plot of the applied load versus relaustion time repersented weeled that dislocation mobility incressed with increasing load, was lower in the To than in the T73 temper, and was higher in the longitudinal direction than in the short-transverse direction, par-Burgarial ticularly at the lower loads.

#### CLERCISION OF CONTRACTOR

A report on the corresion of bervillum has been issued by the Deferse Metals Information Conter.(12) Data are interpreted for corresion in a veriety of environments including atmospheric exposure, acids, alkalis, fresh mater, marine mater, cases, creanic limits, and mouten materials usetals and normetalsi. Stress-crosson cracking, galvanic corresion, and protective coatings are also discussed.

#### CORRUSION OF IRCH-PAGE ALLOYS

## Steels

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The effect of pickling on the properties of HY-130 steel has been studied by the Waval Applied Science Laboratory.(13) Results Indicated that HY-130 could be pickled by the standard Havy HY-80 pickline procedure without impairment of notchtoughness properties, significant attack of the metal, or excessive smut formation. A "drastic" pickle containing des and no inhibitor ampaired the properties of MY-130, but such of each of the properties erties was restored after boiling in water to remove hydrogen.

#### Stairless Strels

Lockheed reports only superficial staining of brazed tubing joints after 90 days' cutdoor es-posure at Yandenberg Air Force Base.[14] Types 321-1/8 H and Type 304 L stainless steel tubing mere induction brazed with Aeroquip fittings (Type 304 L) and ASTM B 260 (82Au-18M1). Specimens were exposed facing the ocean about 300 yards from the water during the calendar period October 26, 1966, to February 16, 1967.

The possible role of corresion-produced hydrogen in the intergranular failures of nonsensitized Type 304 stainless steel fool cladding in boiling-mater-reactor service has been studied by General Electric.(15) Stresset notched tensile specimens were cathodically charged in 4 percent HoSDA containing Aspon. Cracking failures occurred at high tensile loads and were accompanied by severe plastic deformation which probably caused significant lattice transformation from a face- to body-centered cubic structure on preferred crystallographic planes. Cracks were both transgranular and intergranular and were not like those for inservice failures. Failure was most rapid when the load was increased by 10,007 psi increments every 24 hours efter an initial loading of about 25,000 psi. This office was related to nitremen atoms in the metal migrating to dislocation sites and blocking a dislocation "pipe" that might otherwise provide a rapid transport path for hydrogen. in gradual loading, new dislocations were believed to be created in interior regions where some hydrogen had already penetrated because of pravious distocations, thus providing new paths for hydrogen transport.

#### CORRESION OF MACHESTUM ALLOYS

The effect of titanium on the corrosion resistance of magnesium has been reported by Russian scientists.(16) Tests were conducted in 3 percent HaCl solution. The presence of 20,004 percent

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dissolved titanium increased the corrosion resistance of ferrosilicon-extracted magnesim by a factor of 5 L 10. Saturation of electrolytic magnesium with titanium increased its corrosion resistance by a factor of 15 to 20. presumably because of the removal of iron.

#### CORROSION OF NICKEL-BASE ALLOYS

Half-cell potentials have been measured by the Marine Engineering Laboratory for nitel-base superalitys, several pure metals, nitke-i-crossim binary alloys, and several intermetallic compounds in molten NaCl and NagO4 at 1600 F.(17) Platinum was used as the reference electrode. Potentials for pure thromium and alloys convilning more than 15 wt% chromium exhibited a marked positive change with time in the NagOC4 but only a slight positive change in NaCl. The behavior in NagOC4 was correlated with the formation of protective CrOO3 calde on the specience, while that in NaCl was related to the rapid attack on chromium-containing alloys in this medium.

A summary report on the hot corrosion of nickel-base alloys has been issued by Allison Division of General Motors, [18] Each test consisted of 200 cycles at 1700, 1800, 1900, or 2000 F. A cycle consisted of a 0.5-minute spery of 1 percent sodium sulfate solution between 1.5-minute heating periods. A regression equation was derived minth related metal loss to alloy commistry. Chromium and aluminum were beneficial to corrosion resistance whereas tangeten and molybdenum were detrimental. The order of decreasing corrosion resistance of alloys studied was FOR 163, UN-7200, Allay 713C + 20c + Y, Allay 713 + 20c, Inco 717, Allay 713C + 20c + Y, Allay 713 + 20c, Inco 717, Allay 713C, Na-May1 (44.6Cr), IN-100, CMR-233, and Nar-M235.

One years' results of a study of the hot corrosion of nickel-base and cobalt-base superalloys have been summarized by General Electric. (197 Alloys were exposed 500 to 1000 hours at 1600 to 2000 ff to the exhaust gases from diesel fuel (185) which were injected with 5 ppm see salt. Sulfidation was severe at 1600 to 1720 ff, but was not a problem at temogratures above 1720 to 1800 ff, presumably because May504 veporizes at these temperatures. At 1600 to 1750 ff, the commercial cobalt-base alloys were more corrosion resistant than the commercial nickel-base alloys were more corrosion resistant than the commercial nickel-base alloys. The best alloys were May and and dastelloy X. The most corrosion-resistant cobalt-bial alloys at 1900 to 2005 ferer MELECO-29 and -10.

At General Electric, a mechanism study of the hot corrector of superality a in hot gases containing MaCl and 502 led to the conclusion that hot correction was the result of increased oxidation caused by the removal of chronium-rich sulfides. (20) As these sulfides become oxidized, the sulfur penetrated more deeply into the alloy, creating susceptibility to faster oxidation in their wase. Aluminum, certum, and titanium additions to nickel-base allows reduced corrosion in some instances, whereas carium, lantharum, and yttrium were beneficial in cobaltbase alloys.

### CERCSICH OF TITANICS

# General

The English have studied the ignition and burning of titanium alloys in connection with fires

in the titenium compressor stages of gas turbine engines, [21] Some 39 binary alloys were ignited in crypen. The ignition temperature of pure titenium was found to be leif G (2283 F). Significant changes in ignition temperature due to alloying are summarized below.

| Alloy Composition. | Difference from Igni-<br>tion Value for G. P.<br>Titples G |
|--------------------|--|
|                    |  |
| 6 copper           | +63  |
| 5 iron             | +70  |
| 34 aclybdenus      | *85  |
| 6 mickel           | +63  |
| O.1 sulfur         | 198  |
| C.S silicon        | +78  |
| 2 silicon          | +90  |
| 46 tantalum        | +96  |
| 30 tungsten        | +98  |
| 10 silver          | -54  |
| 13 copper          | -fd  |
| 12 manganese       | -117   |
| 0.25 sulfur        | -57  |
| 12 tin             | -115   |
| 22 tin             | -107   |
| 31 zirconium       | -267   |

Although aluminum in titonium had no significant effect, the injection of aluminum powder into the stream lowered the ignition temperature by more than 100 C, thus tending to confirm that fires in titanium compressor blades are caused by rubbing against debris from aluminum blades in earlier stages of the compressor.

#### Stress-Corresion Cracking

The proceedings of the 1-day seniner at Battelle's Columbus Laboratories on March 6, 1967, dealing with accelerated crack propagation in titanium has been issued by the Driemse Metals Information Center, (22) Included are 15 information pepers and discussions by participants on the strese-corrosion cracking of titanium alloys by machamol, halogenated hydrocarbon, and other spittlows.

The corrusion behavior of II-AAI-W in commercial freen IF with and without 0.3 ppm chlorine gas has been studied by Aerospace Corporation. [23] Metallographic analysis and mechanical-property measurements revealed no cracking after 72 hours' exposure of melded and nonmelded teneils specimens stressed to 80 percent of the 0.2 percent offset yield strength.

The stress-corrosion-cracking behavior of some 30 Commercial titanium silops has been described by the Havel Research Laboratory to previde guideline information and determine the underlying principles that effect stress-corrosion cracking. (24) Tests were conducted in 3-5 percent RGCI solution with pre-cracked cantilever been specimens. Beld specimens were included in the program. The results indicated that there was no correlation between mechanical properties and susceptibility to stress-corrosion cracking.

Fracture trushness and the stress-corrosion cracking of welded 1-inch thick titanius-siloy specimens has also been studied by the Havel Basearch Laboratory. (22) The stress-corrosion tests were performed in 3.5 percent MacI solution using precrated canti-ever bem specimers. Allows studied included Ti-6A1-8; Ti-6A1-3Do, Ti-6A1-67-2Bn, Ti-6A1-3Ph, Ti-6A1-3Do, Ti-7A1-3D-17; Ti-6A1-3Dm20-27; Ti-7A1-3Dn, and Ti-6A1-2D-18-0.880. There did not appear to be any correlation between fracture toughness and stress-corresion-cracking resistance of the materials.

Studies on the effect of hydrogen and microstructure on the stress-corrosion cracking of litanium allows are continuing at Douglas, 200 Different amounts of hydrogen (27 and 100 pres) were introduced in 11-861-Min-IV at 1000, 1000, and 2000 F, followed by an air quench. Subsequent tests with notiched speciesms in ambient 3 pacernt NGCI solution revealed that the 1000 F solution treatment was susceptible to atress-corrosion cracking at these hydrogen concentrations, but that the 1800 and 2000 F treatments were nct.

The morphology of stress-corrosion cracks in titanium allows has been studied by Scring.277 Precracked specimens were exposed to J.5 percent MaGI rivition. Comparisons of electron firstographs of cracks and electron micrographs of tracks and electron micrographs of the structures in alpha-beta Ii-841-1Mo-1/ and Ii-641-48 alloys revealed a cleavage failure in the alpha phase and a ductile runture in the beta phase. Copland dislocation arrangements were found in II-641-49 and II-841-1Mo-1/ but not in II-441-49-0-1/, which corralated qualitatively with susceptibility of these alloys to cracking under these exposure conditions.

The stress-corrosion-cracking behavior of Ti-6AI-Mo-IV alloy in NaCl and methanol is being studied at the Chio State University, [23] Slow crack growth in precracked tensile-type specimens occurred over a range of -900 to 2000 my (SiE) in salbmater, suggesting that hycrogen evolution is not a necessary factor in crack propagation. Current densities of 1.5 mmp/cm<sup>2</sup> were estimated during the active propagation of a rapidly advancing crack in methanol-mater-salt solution.

The influence of alcrostructure on the stress-corrosion fracture path in titanium alloys is being studied at Boeing, [-2] Results obtained with pre-cracked notified specimens in 3.5 percent NACI solution indicated stress-corresion-reacking susceptibility in the siphs phase in II-8A1-180-19, II-6A1-49, and II-6A1-30-19, in meartensive in II-6A1-12, 3.50., and in the beta phase in II-13Y-11CT-3A1. Stress-corresion-cracking susceptibility could not be correlated with any one or combination of alcrostructural features. Immunity to cracking (at least in the three immune phases of II-6A1-180-19 alloy) appeared to be related to high solybdenum and varieties controlled.

Bosing has also used wedge-force loading of contex-casched sheet speciamen to determine weather stress-corrosion cracking depends on an applied crack-tip stress-intensity factor or no net-section stresses. (20) Bith this loading, crack extension causes a decreasing stress-intensity factor at the crack tip, while the net-section stresses increase. Thus, when the stress-corrosion crack growth is arrested in this speciamen, the dependency on stress intensity is indicated. The stress intensity at arrest for II-9AI-1Borly Wallow gareed well with X<sub>2</sub>cc

values determined by other techniques that establish crack initiation thresholds through multiple tests.

Research on the stress-corresion cracking of notiched titanium in semmeter is a cticular at the Marine Engineering wabpretory. 3. Pessets to date with titation-e. ....... e...... indicate that a critical amount of congrent [1:A] precipitate will cause semmater stress-corrosion cracking. As the quantity of Ilial was increased, the sensitivity of the accor to cracking also increased. The reduction of alminum and oxygen contents and the addition of isomorchous bets stabilizers suppressed the formation of FinAl and improved the resistance of titaniumaluminum alloys to cracking in sepaster. Minor additions of less than 0.5 percent of the extectoid formers, mickel, iron, and mangenese, increased the cracking sensitivity of Ti-7A1-2Cb-17s, mails the addition of 0.07 percent calledium made this same allow resistant to cracking. A minimum of 0.250 percent exygen in unalloyed titanium induced cracking in sewester.

The effect of high-sitiude supersonic air flow conditions on the hot-salt cracking of titanium has been investigated at Lockheed. 120 Hind-tunnel tests were conducted for a total of 50 hours exposure under sach 2.0 supersonic flow conditions at a pressure equivalent to 70,000-ft altitude and temperatures of 600 and 700 F. Dublex-annealed TH-AAI-44 alloys were used in self-stressed specimens. The results demonstrated that these simulated supersonic-filight conditions did not eliminate hot-salt cracking. However, the cracking was not as severe as in static laboratory tests at the same recoverature, presumbly because of the removal of some of the salt coating by the high velocity air.

A summary report has been issued by Northron on the hot-selt stress-corrosion cracking of II-6Ai-47, Ti-8A1-1Mo-17, Ti-13Y-11Cr-3A1, Ti-6A1-6/-2Sn, and Ti-679 elloys, 33) At 450 F. only mill-ennested Ti-BAi-1Mo-1V slicy exhibited cracking. Threshold values for cracking were found to be between 0.35 and 0.50 of the yield strength at 550 F and between 0.25 and 0.45 of the yield strength at 650 F. At stress levels just above threshold values, crack nucleation times were much langer with thermal cycling than during con'invous exposure at temperature. Studies on the kinetics of the formation and decomposition of TiCl2 on NaCl-coated titanium ailove indicated the possibility of eliminating the hot-sait cracking of titanium alloys above 550 F by thermal cycling in such a manner that the time at temperature is less than that required to form TiClo and that the time at room temperature is greater than that required to decompose IiCl2.

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